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# SODIUM DIFFUSE BANDS IN LOW-PRESSURE HOLLOW CATHODE DISCHARGE SPECTRA

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We report observation of two distinct $Na_2$ violet continuum emission bands peaking at 436.5 and 452.0 nm obtained in discharge with hollow cathode electrodes configuration in heat pipe oven.

## *1. Introduction*

The violet sodium emission bands extending between 410 and 460 nm have been known for about 60 years, when the first observation was made using sodium arc[1]. However, population mechanism of the relevant states in certain type of the discharges still has no satisfactory explanation.

We report the observation of the sodium dimmer diffuse band from a low-pressure sodium discharge. Sodium vapour has been generated in a standard heat-pipe oven (HPO) with hollow cathode electrode configuration where HPO tube served as the cathode and 0.1 mm molybdenium wire stretched along the axis of HPO served as the anode. Using this configuration we were able to select between two modes of operation — the hollow cathode type discharge (HCD), which is basically a glow discharge, and the other one, spatially inhomogeneous, »quasi-arc« discharge (QAD). Spectra of these two types of discharges appear rather different. In HCD mode of operation, sodium resonance line and A-X and B-X bands are overlapped with some ArII and ArI lines. In QAD mode the most prominent spectral features are sodium resonance line and two violet continuum bands.

These two continua we recognized as the sodium »diffuse band« at 436.5 nm, and »interference continuum« at 452.0 nm. According to the recent LIF experiments of Pichler et al.[2] these bands must be originating from $2^3\Pi_g$ and $2^1\Sigma_u^+$ states of $Na_2$, respectively. These bands have been also observed in laser emission with single- or multi-photon excitation in a wide variety of experiments[3,4]. $2^3\Pi_g - 1^3\Sigma_u^+$ and $2^1\Sigma_u^+ - X^1\Sigma_g^+$ transitions have been proposed as a candidate for laser action[5]. Recently Bahns and Stwalley[6] provided some gain measurements in order to achieve a new tunable excimer laser in the violet. They observed significant gain through stimulated emission in the violet when sodium vapour has been pumped using the 350.7 nm line of a $Kr^+$ laser.

## 2. *Experimental setup*

The experimental setup is shown in Fig. 1. The discharge from the center of the linear heat-pipe oven was imaged onto the entrance slit of the scanning monochromator and detected by means of the Hamamatsu R955 photomultiplier tube. Signal was processed by a lock-in amplifier and recorded on strip-chart recorder.

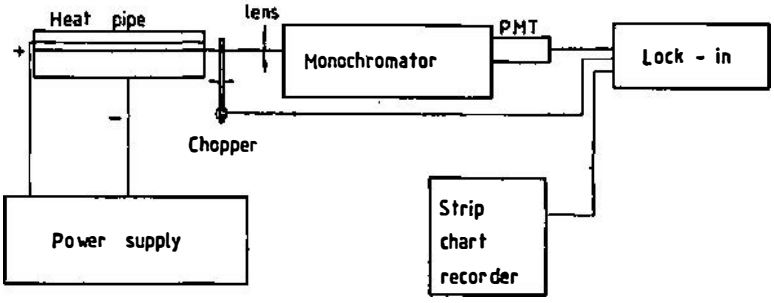


Fig. 1. Schematic diagram of the experimental setup

The argon pressure in heat-pipe oven was varied between 100 and 500 Pa but the best results were obtained in pure heat-pipe mode of operation at $T = 520\,°C$ and $p_{Na} = 100$ Pa. Effective sodium vapour column was about 10 cm. We chose the electrode configuration consisting of a molybdenum wire (0.1 mm in diameter) as one electrode and heat-pipe oven body (32 mm inner diameter) as a second electrode. To prevent condensation of sodium on the molybdenum wire, it was separately heated by the electric current from a stabilized power supply. Heat-pipe oven body served as the cathode in HCD. The voltage applied between the anode and cathode was varied between 100 and 150 V, and discharge current was varied in the range from 10 to 150 mA. We, also, operated HP with split wick configuration and obtained the same spectrum and current-voltage dependence.

The electrode arrangement enables the choice between the positive corona discharge (configuration HCD) and the negative corona discharge (configuration HAD — hollow anode discharge). Positive corona discharge (wire positively charged) was preferable for observation of sodium diffuse bands in »quasi-arc« discharge

mode. Visually, it reminds on extended yellow arc between wire and HP body. Discharge was located in a small volume near the centre of the heat-pipe oven. The burning of the discharge plasma was relatively stable, but the chatode »spot« region was randomly moved around the inner wall of the heat-pipe oven, while the anode »spot« region was fixed. Power requirements to operate »quasi-arc« discharge are the same as for HCD. That means that HP can operate in one of these modes with same power input, but if we desire to switch from »quasi-arc« discharge into HCD we must increase discharge current. The increase of discharge current causes broadening of this »arc« in region near HP wall and as a final consequence tranformation into HCD.

In HCD configuration we observed bright glow discharge which fills the whole interior of heat-pipe oven. Additionally, in cooler regions, where we have mass of condensed material, appears glow discharge in argon-sodium mixture which require higher discharge voltage.

## 3. *Results*

In Figs. 2a and 2b we present the results of spectroscopic observations of both modes of operation.

HCD spectrum (Fig. 2a) is dominated by sodium resonance line, A-X and B-X bands, still covered by ArII lines. All other spectral features are masked by strong argon lines.

Fig. 2b exhibits different spectral features. There are sodium atomic lines from the sharp and diffuse series, well known $Na_2$ A-X and B-X band structures, and first resonance line at 589.2 nm. Beside these spectral features we observed diffuse emission bands peaking at 436.5 and 452.0 nm. Position in the spectrum and overall shape of these bands agree well with results of a recent LIF experiment of Pichler et al.[2]. We interpret these continua as stemming from $2^3\Pi_g - 1^3\Sigma_u^+$ and $2^1\Sigma_u^+ - X^1\Sigma_g^+$ transitions, respectively. The intensity of diffuse band as compared to the B-X band is about the same but compared to the A-X band is nearly 30% stronger. The absorption in the region of interest was rather low due to the low density of sodium vapour[13].

We investigated the influence of the HCD discharge power input to the behaviour of violet bands. Pressure of buffer gas was kept at the same value in all measurements. Peak intensities of diffuse band ($I_{436}$) and interference continuum ($I_{452}$) are plotted versus voltage (Fig. 3) (at constant discharge current) and current (Fig. 4) (at constant voltage), together with intensity ratio ($R = I_{436}/I_{452}$). Fig. 3 shows that intensity of both bands rises in the same ratio with the increase of the applied voltage. In Fig. 4, peak intensities decrease with the increase of the discharge current, but the intensity ratio remains constant while current is changed.

## 4. *Discussion*

In Fig. 5 we present potential energy curves[8,9] for various states of the $Na_2$ molecule, and relevant difference potential curves. Two transitions involving in-

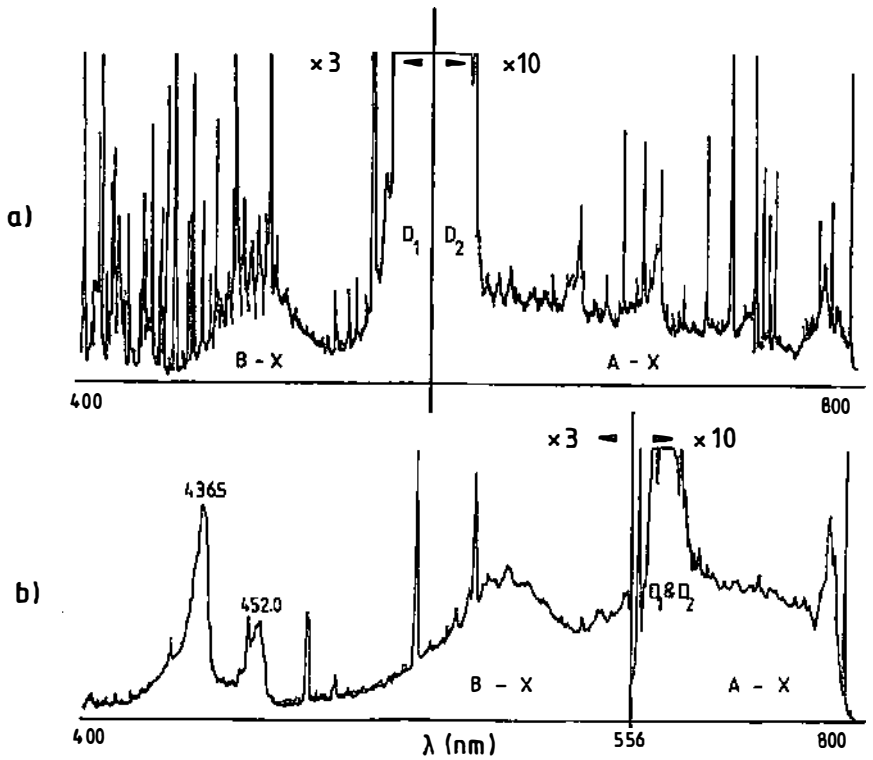


Fig. 2. Emission spectra from HCD (a) and QAD (b). $Na_2$ diffuse band and interference continuum have a peak at 452.0 and 436.5 nm, respectively. The spectrum (a) was observed using constant scanning speed while scan (b) has a change in scanning speed. The spectrum was not corrected for spectral sensitivity of detection system.

dicated potential curve contribute to the structured continuum in the spectral region between 410 and 460 nm. The first system corresponds to the transitions between singlet states ($2^1\Sigma_u^+ - X^1\Sigma_g^+$) giving so called »interference continuum«. Analysis of the singlet difference potential curve shows that the minimum in the relevant difference potential corresponds to the wavelength of 452.0 nm. The outer well in the double minimum potential curve (Fig. 5), $2^1\Sigma_u^+$, enhances the peak at 452.0 nm through the influence of the Boltzmann factor in the emission coefficient.

The second system corresponds to the triplet transition ($2^3\Pi_g - 1^3\Sigma_u^+$) and it is often called the »diffuse band«. Corresponding difference potential curve possesses two extrema, what explains shape of this diffuse band. We attribute main peak of the observed diffuse band (at 436.5 nm) to the minimum, and shoulder at about 428 nm to the maximum in the difference potential curve. The contribution of the B-X band appears as a weak continuum which monotonously decreases towards violet.

Due to the coaxial electrode configuration, we may have two maxima in electron energy distribution function[10] and we expect generation of »slow« and »fast«

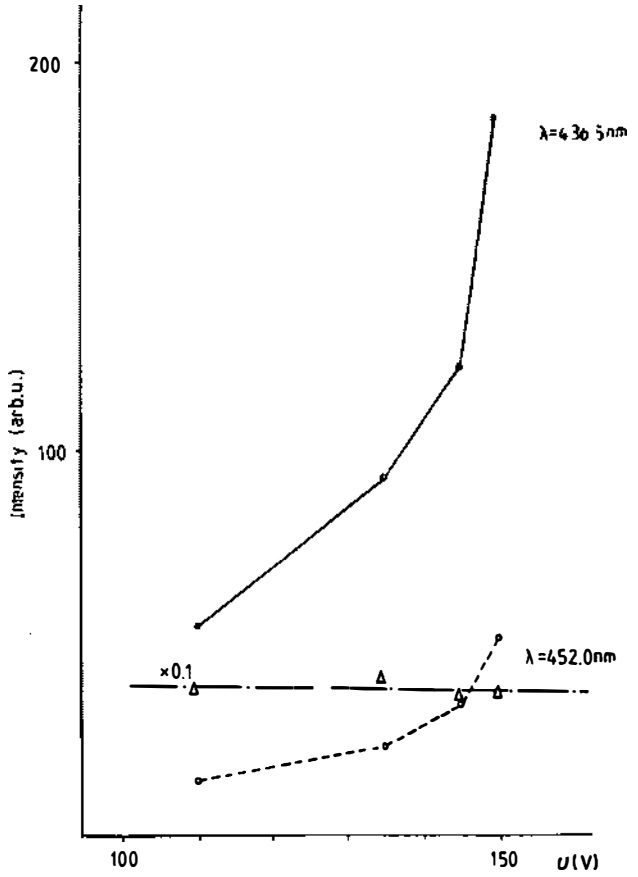


Fig. 3. Diffuse band and interference continuum peak intensity versus discharge voltage. Buffer gas pressure $p = 100$ Pa, discharge current $i = 55$ mA. $R = I_{436.5}/I_{452.0}$ (—·—·).

electrons with peak kinetic energy of about 0.5 eV and 5 eV, respectively. Fast electrons should excite molecules to upper states, and slow electrons distribute molecules between rotational-vibrational states within upper electronic states[10]. Moreover, we have additional mechanism proposed in Ref. 11 where authors assume that excited $Na_2$ molecule is produced in collisional process with two 3P-excited atoms.

Figs. 3 and 4 show no influence of different discharge conditions on peak ratio. The electron distribution is shifted towards higher energies (Fig. 3) due to the increase of applied voltage, what may affect simultaneous rise of both peak intensities. On the other hand the peak intensities drop with increasing discharge current (Fig. 4) in the same power input region as in prior case. In this experiment we were not able to distinguish if this behaviour is caused by increase of discharge volume, change of electron excitation rate, or chage of electron energy distribution function. The decrease of peak intensities with increasing discharge current may

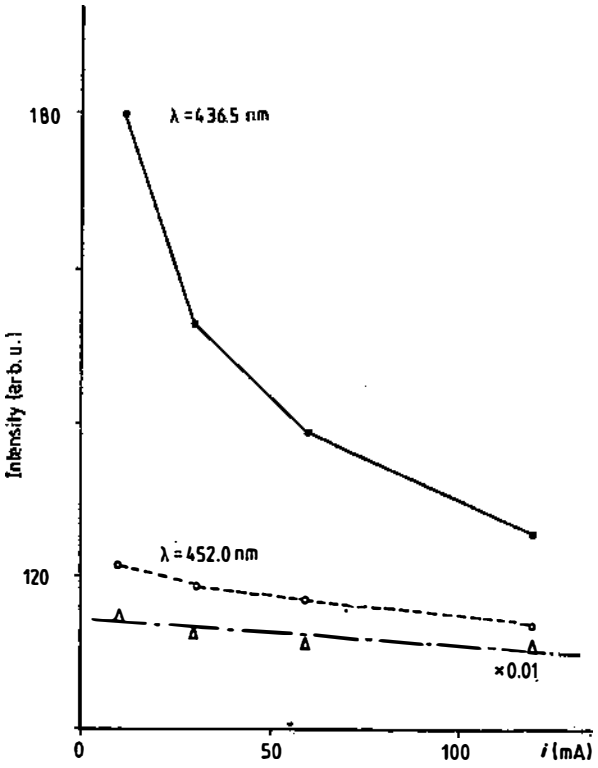


Fig. 4. Diffuse band and interference continuum peak intensity versus discharge current. Buffer gas pressure $p = 100$ Pa, discharge voltage $U = 130$ V. $R = I_{436.5}/I_{452.0}$ (—·—·).

be induced by suppressed excitation rate and by the deactivation of relevant molecular state. Under our experimental conditions, taking into account effect of electron focusing, the most dominant mechanism may be deexcitation of sodium molecules by electron impact due to the increase of current density. Quenching by electron impact is the most effective process of destruction of excited molecules. Other possible mechanism proposed by Rebbeck and Vaughan[7] is the increase of ionic fields which could mix upper level with adjacent levels allowing depopulation through this channel. But, this cannot explain rather sharp fall-off of experimental curve in Fig. 4 (Ref. 12) because intensities of other molecular bands (A-X, B-X) do not exhibit such anomalous behaviour. Beside quenching by electron impact, the spontaneous radiation and quenching of excited molecules by sodium and noble gas atoms should be taken into consideration. Ratio of ($R$) remains constant what indicates a large mixing of the relevant upper states.

## 5. *Conclusions*

Our results indicate that $Na_2$ violet bands originate in collision processes of $Na_2$ with electrons. Electron energy distribution function probably has two maxi-

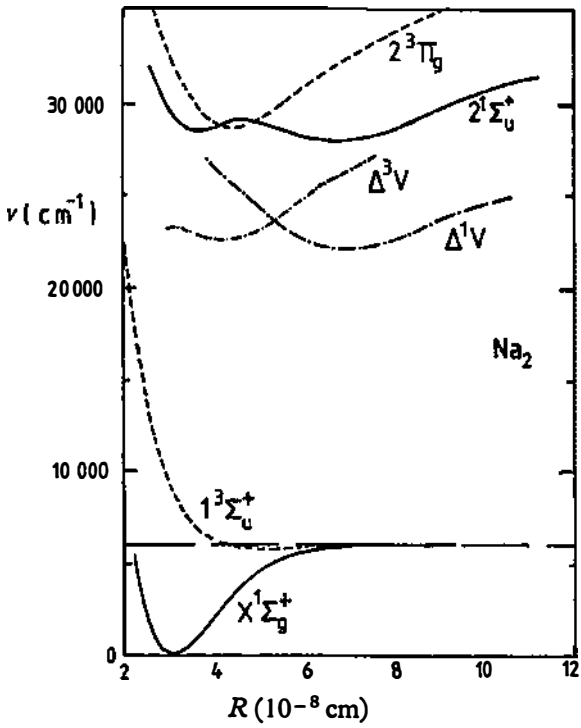


Fig. 5. $Na_2$ potential energy curves showing molecular states of the interest, and relevant difference potential curves.

ma, what may help in further discussion of the population mechanism. In electrode arrangement used in our experiment we have focused electrons which populate upper molecular states and destroy excited molecules with different excitation and deexcitation rates. Collisional energy transfer (e. g. $C^1\,\Pi_\mu \rightarrow J^3\,\Pi_g$ state) may play an important role and should be taken in to the future considerations. The proposed model for population of upper level should be considered as a qualitative one and implies further work on discharge either in HCD configuration or HAD configuration, where in the latter case we have defocusing effect on electrons.

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## NATRIJEVE DIFUZNE VRPCE U SPEKTRU NISKOTLAČNOG IZBOJA SA ŠUPLJOM KATODOM

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Koristeći spektroskopsku toplovodnu peć u kojoj su bile smještene elektrode u konfiguraciji šuplje katode istraživali smo spektar natrijevih para u izboju na tlaku od 100 Pa. Istraživali smo ovisnost intenziteta i oblika strukturiranih kontinuuma u plavom dijelu spektra o parametrima izboja.